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SENSITIVITY OF METAL-HALOGENATED SOLVENT COMBINATIONS

G. D. Artz and [illegible]

Research Division
ROCKETDYNE
A Division of North American Rockwell Corporation

For Presentation At

INTERAGENCY CHEMICAL ROCKET PROPULSION GROUP MEETING

HAZARDS WORKING GROUP

El Paso, Texas

5 December 1967

SENSITIVITY OF METAL-HALOGENATED SOLVENT COMBINATIONS

Impact sensitivity tests were found to be beneficial in determining the sensitivity of barium/Freon TF combinations. Because of the widespread use of halocarbons and potentially reactive metals within the Aerospace and Systems Group of North American Rockwell Corporation it was deemed prudent to extend the impact sensitivity experiments to include a series of metals and halocarbons currently in use.

Literature surveys disclosed that very little has been written in the general chemical field on barium and its reactivity. Only when the literature surveys include the pyrotechnics and explosives areas do we begin to find indications of the explosive reactivity of barium and halocarbons. This same literature survey also disclosed that granular metals other than barium have on occasion reacted unexpectedly and explosively with halogenated solvents, including aluminum powder with carbon tetrachloride and aluminum powder with trichloroethylene. This type of behavior of powdered or granular metals after exposure to supposedly "safe" solvents raises considerable doubt about their safeness". The program described herein was conducted to determine just how sensitive to impact various metal/halocarbon slurries are, and to determine, if possible, if a potential hazard (due to impact) exists in the handling of more common powdered or granular metals in contact with a variety of commonly used halogenated solvents. The combinations chosen for this program are representative of the kinds that are in general use; they include some combinations known to be or likely to be used in

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manufacturing or laboratory operations at North American Rockwell Corporation. Ten different kinds of metallic powders or granules were tested with six different solvents, giving a total of sixty combinations. A brief description of these particulate metallic materials and solvents is as follows:

METALS:

Aluminum Powder	-	Reynolds No. 1-511 Atomized Powder, 13 ± 3 microns, Reynolds Metals Company
Mg Powder	-	30/50 Mesh Atomised, Harshaw Chemical Corp.
Ti Powder	-	Laboratory sample labeled " +325 mesh", origin unknown.
Ba Shavings	-	Shavings produced by cutting up nominal 1 mm x 3 mm granules, Alfa Inorganics, Inc.
Li Shavings	-	Small shavings cut from an ingot, Lithium Corp. of America.
Be Powder	-	Fine Powder (size unknown) Brush Beryllium Corp.
BeH_2 Powder	-	Fine Powder (size unknown) Ethyl Corp.
Aluminum Filings	-	Filings produced with a coarse rasp from a sheet of commercial aluminum (grade unknown).
Magnesium Filings	-	Filings produced with a coarse rasp from a sheet of commercial magnesium (grade unknown).
Boron Powder	-	95+% Purity, average particle size less than 1 micron, American Potash and Chemical Corp.

SOLVENTS:

Freon MF CCl_3F	-	Monofluorotrichloro methane, E. I. duPont
Freon TF $C_2Cl_3F_3$	-	Trichlorotrifluoro ethane, E. I. duPont
Carbon Tetrachloride CCl_4	-	Mallinkrodt Chemical Works, Analytical Reagent (Low Sulfur)
Trichloroethylene C_2HCl_3	-	Mallinkrodt Chemical Works, Analytical Reagent

Solvents - (Continued)

Perchloroethylene C_2Cl_4	- Tetrachloroethylene, Matheson Coleman and Bell, Spectroquality Reagent
1,1,1 Trichloroethane CH_3CCl_3	- Methyl chloroform, Matheson Coleman and Bell, Technical Grade

The impact sensitivity test apparatus used on this program is a slight modification of the Jet Propulsion Laboratory (JPL) impact sensitivity tester. Basically, the test is conducted by putting a small sample (a few milligrams) of the material to be tested inside a shallow depression in a hardened steel anvil, then dropping a steel ball of a known weight from a measured height so that it strikes a hammer which is in contact with the sample. A "go" on this tester is evidenced by either a flash or a loud noise or both. By increasing the drop height after each "no go" or lowering the height after a "go" it is possible to get some idea of the impact sensitivity of the material being tested. The sample is changed after each "no go" so that a fresh sample is used for every test.

Most of the many kinds of testers in current use appear to give a different impact sensitivity value for the same material. For this reason it is generally necessary to reference the results obtained for a new material against some well-characterized material tested on the same impact machine. This type of comparison is more meaningful than an absolute value stated in some units of weight x height would be, even though these absolute values are often quoted (for a given type of tester) as an indication of the impact sensitivity of a material. The reference material used in this program was Composition B, a high explosive consisting of a blend of RDX and TNT with a small amount of wax added.

Most of the metal-solvent combinations tested were run in an identical manner. A quantity (not weighed) of the powdered or granular sample sufficient to fill the cavity in the anvil was used in each test. Then the solvent was added in excess and allowed to remain in contact with the powder for about a minute prior to dropping the ball. Where solvent had a tendency to evaporate, especially evident with Freon MF, additional solvent was added at intervals so that an excess was present at all times up to the time of impact.

With tests involving barium it was believed desirable because of the reactivity of barium with oxygen and moisture to minimise or eliminate exposure to air prior to the impact of the ball*. Accordingly, whenever barium was handled it was always done in an argon atmosphere up until the sample could be "drowned" in the solvent. Lithium, also reactive, was cut into shavings under an argon atmosphere but less care was taken to exclude air in subsequent operations. An attempt was made to minimise exposure to air of the aluminum filings and the magnesium filings by producing only enough filings at one time for a few tests, then testing them very quickly afterward. In all the other tests no attempt was made to exclude air from the metals at any time.

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*There is some evidence that moderate exposure of barium to air does not materially affect its sensitivity. Prior to running this present series of 60 combinations, it had been found in an earlier test that the barium-Freon TF combination in which no attempt was made to exclude air after the barium had been cut into shavings gave flashing at a [illegible]-inch height with a 5-pound ball. This compares very closely with the value of [illegible] inches with the same 5-pound ball, found during the current tests where air exposure was eliminated. The difference between the [illegible]-inch height and [illegible] inch height is considered to be of little significance, probably well within the experimental range of values to be expected from this type of test.

The maximum drop height capability of the test apparatus employed is 50 inches. With a 5-pound ball, any material that fails to show any reaction at 50 inches is usually considered to be relatively insensitive to initiation by impact. (Composition B, previously mentioned as our reference material, showed a 50% probability of detonating at 8 inches on our tester.)

Ordinarily the impact sensitivity heights reported in the literature are 50% probability levels, although in some instances the height given is the 10% probability point. Both levels are arrived at by some up or down system (normally Bruceton series) of varying the height from test to test and require that fairly large numbers of tests be run. In the current program the objective was more concerned with determining the approximate minimum height at which a reaction occurred, rather than determining the statistical probability of this event occurring. Because of the limited number of tests run on each combination, it is reasonably certain that the minimum heights given for many of the combinations in Table I are higher than would have been obtained had a larger number of samples been tested.

The maximum height of 50 inches was utilized for the initial testing of most combinations. If three consecutive "no go's" resulted, it was presumed that this particular combination was insensitive to impact and no further tests were run on this combination. If any of these initial three tests produced a detonation or flash, the height was progressively reduced until a height was reached where three consecutive tests failed to give a go, at which point testing of that combination was stopped. Therefore the values given in Table I are those heights at which a reaction occurred at least once out of three attempts.

Looking at Table I, a number of things are evident. Probably the most evident is that combinations with barium are definitely the most sensitive of all the combinations tried. This sensitivity, greater even than lithium combinations, is at first glance very surprising, since lithium is a member of the extremely reactive alkali metal series, and is higher in the electromotive series than barium. However, the German references also showed the barium slurries to be both more sensitive to initiation and more violent in their reaction than lithium slurries with the same halocarbon. The value of 4 inches at which a flash occurred (as mentioned previously, an earlier series of tests had given a value of 3 inches) indicates that the barium-Freon TF combination is a very hazardous one. In fact, Freon TF combinations were among the most reactive with all the metals tested.

The term "detonation" as used here indicates that a loud noise, usually accompanied by a bright flash and smoke, were produced. There was also a strong pungent odor produced, and the test apparatus and immediate vicinity were covered with a film of gray or black material. None of the original sample was found in the apparatus.

Where only flash or heavy sparking was recorded, the only noise that could be detected was the background noise produced by the impact of the ball striking the test apparatus. In these instances part of the original test sample was found to be still in the apparatus, just as it was when there was no evidence of a reaction.

Table I shows that none of the metals gave a positive reaction with 1,1,1 trichloroethane (methyl chloroform). This might indicate that this would be a safe solvent to use. Unfortunately, this conclusion is not necessarily a valid one. Although the tests show that 1,1,1 trichloroethane is safer,

its composition is very similar to some of the other solvents, so that under the proper conditions it might react much as these other solvents do.

Based on the results of this program and on the limited, brief literature search, there is a definite potential hazard in handling granulated metal-halogenated solvent combinations. Serious consideration should be given to the use of nonhalogenated solvents whenever possible, even if it means increasing the flammability hazard of the operation. Adequate measures (ventilation, inert atmospheres, grounding, etc.) can usually be taken to reduce this flammability hazard.

The use of an ever-increasing variety of new metals and alloys in industry may produce some very sensitive combinations if these materials are exposed to halogenated solvents. Before any halogenated solvents are used with powders, shavings, chips, etc. of these new metals or alloys the reactivity should be determined by some sort of impact sensitivity tests as a minimum requirement. It might be wise to run other sensitivity tests as well, since a combination which appears to be insensitive to impact may be sensitive to another mode of initiation.

These precautionary measures with halocarbons are probably not necessary when handling large pieces of sheet metal, billets, castings, or machined parts, *if* proper care is taken to previously ensure the removal of chips, cuttings, filings, and grindings from the parent material.

TABLE I

MINIMUM IMPACT SENSITIVITY HEIGHT (inches)
(5-lb Ball)

SOLVENT	METAL									
	Al Powder	Mg Powder	Ti Powder	Ba Shavings	Li Shavings	Be Powder	BeH_2 Powder	Al Filings	Mg Filings	B Powder
Freon MF	F,50	0	0	X, 20 F, 15	X, 50 F, 40	0	0	0	0	0
Freon TF	F,50	0	F,50	X, 10 F, 4	X, 20	0	0	0	0	0
Carbon Tetrachloride	X,50	F,50	0	X, 15 F, 10	X, 18	F, 50	0	0	0	0
Trichloroethylene	0	F,50	F,50	X,15 F,13	X,25	F, 50	0	0	0	0
Perchloroethylene	0	0	0	X, 20 F, 15	X, 30	0	0	0	0	0
1,1,1 Trichloroethane	0	0	0	0	0	0	0	0	0	0

X, Number - Height in inches at which detonation occurred.
0 - No reaction at 50 inches.
F, Number - Height in inches at which flash or heavy sparking occurred.